# PATENT SPECIFICATION

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(19)

## (54) A PHOTOCHEMICAL METHOD OF PREPARING HYDROCARBON DERIVATIVES

(71) We, SOCIETE NATIONALE DES PETROLES D'AQUITAINE, a French Company, of Tour Aquitaine, 92400 Courbevoie, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns photochemical processes to prepare halogen or sulphohalide substitutes or hydrocarbons and mercaptans. Methods of preparing chlorides, sulphochlorides or mercaptans exist in which the gaseous reactants form part, either wholly or partly, of a liquid phase. In one of these processes, described in F. Asinger's book "Paraffins, chemistry and technology", Pergamon Press 1968, pp. 520 *et seq.*, propane or butane sulphochlorides are prepared by bubbling the gaseous mixture of hydrocarbons, chlorine and sulphur dioxide through a solvent such as carbon tetrachloride. The reaction takes place within the solvent, which dissolves the sulphochloride that forms. The reaction heat that is given off is removed by means of an internal circuit through which a cooling agent flows.

This sulphochlorination process fails to offer satisfactory results in the case of methane, and yields are low, mainly because of the low solubility of methane in the solvent that is used. In addition, since the final product is soluble in the solvent medium, it has to be separated by fractional distillation. Because of the exothermic nature of the reactions, the reactor that is used must be large enough to allow a cooling coil to be fitted inside it. This may be incompatible with the value of the optical path calculated for optimum efficiency, in view of the light absorption coefficient of the medium.

Unlike existing processes in which the reaction takes place between the reactants dissolved in a liquid phase, reactions described in this invention take place between undissolved gaseous reagents, while an inert liquid phase, acting as heat exchanger, covers the whole section of the reactor in the form of a shower of droplets. It has also been found that in some cases this liquid phase not only acts as heat exchanger, regulating the reaction temperature, but also helps to control and limit the propagation of undesirable secondary reactions, resulting from radicals formed by photolysis, by deactivating radicals on the surface of the droplets, providing much higher yields and conversion rates than those obtained with other photochemical processes.

According to this invention, we provide a photochemical process for preparing a halogen-substituted hydrocarbon from an olefin and a halogen source by an addition reaction, a sulphohalide-substituted hydrocarbon from a hydrocarbon, $SO_2$ and a halogen, and a mercaptan from an olefin and $H_2S$ by an addition reaction wherein all the reactants are passed through an irradiated reactor in gaseous form, in contact with a dispersed liquid phase comprising at least one liquid which is inert and is substantially incapable of dissolving the reactants the liquid phase being fed in at the top of the reactor in the form of a shower of droplets, and, passed through the reactor, so that it reaches the whole of the section of the reactor which is in contact with the gaseous mixture, the liquid which has passed through the reactor being treated to separate out the products of the reaction.

The liquid from which the reaction products has been removed may be passed through a heat exchanger and recycled to the reactor.

Preferably, the reaction product is insoluble in the liquid phase.

Depending on the synthesis involved, this liquid phase may consist of an aqueous solution of inorganic salts or acids, which will not dissolve the hydrocarbons used, such as olefins, and which have a negligible dissolving effect on the other reactants in the reaction, such as $SO_2$ and $Cl_2$. Polar organic phases such as inferior alcohols or glycols may also be used, because of their slight or non-existent dissolving effect on hydrocarbons and halogens.

The advantage of this process is that,

depending on the nature of the liquid phase, it may simply draw off the reaction products, to prevent an extended stay in the reactor, which could cause degradation of the product, or extract them selectively from the medium in which they form. It can also act as a vehicle for certain gaseous, liquid or solid reagents, dissolved or undissolved. In the presence of the gaseous phase, the liquid phase, in the form of a shower of droplets, also acts as an effective heat exchanger, without reactors having to be of a size incompatible with other parameters involved, and removing the need for an exchanger system which would absorb light.

This new process can be applied to many different reactions. They include, among others, photochemical processes for preparing methane sulphochloride, of 2,2 - trichloroethylene from vinyl chloride, or of mercaptans from olefins, in the form of gas or vapours, and $H_2S$.

The following example involves photosynthesis of methane sulphochlorides; this will illustrate the process, which is however in no way restricted to this example.

The installation illustrated in the accompanying figure comprises a reactor 8, 1 m in diameter and 3 m in height, containing a submerged 120 W mercury-vapour lamp. The top of the reactor contains a perforated sheet of Teflon (Registered Trade Mark), which distributes the liquid phase fed in through pipe 13. The installation also comprises a decanter 11 and storage tank 14 for the methane sulphochloride produced.

The gaseous reactants, methane, chlorine and sulphur dioxide, are fed in through pipes 1, 2 and 3, into a mixer 7, which also receives the effluents $SO_2$ and $CH_4$ from the recycling point 6. This gaseous mixture is then fed into the reactor through pipe 5. A 65% sulphuric acid solution is fed in at the top of the reactor, through pipe 13. It is divided into thin jets as it passes through the perforated sheet, and falls in a shower of droplets over the whole section of the reactor, washing and cooling the gas. The liquid phase leaving the reactor draws off the methane sulphochloride that has formed, as well as gaseous reagents that have not reacted, and the mixture reaches the decanter 11, where the methane sulphochloride is separated by gravity and leaves along pipe 12. The gas given off in the decanter is dispatched to a mist separator 10. A gaseous mixture of $CH_4$, $SO_2$, $Cl_2$ and HCl leaves this separator along pipe 9, for treatment in another part of the installation (not shown here), to remove the HCl before recycling the gas along pipe 6.

The liquid phase leaving the decanter passes through a heat exchanger, which keeps its temperature at approximately 20°C, on its way to the reactor.

In the initial stages, the liquid phase preferably contains 55% sulphuric acid. As it absorbs $SO_2$ in the presence of $Cl_2$, this concentration rises, and it is not until it reaches 65% that the methane sulphochloride floats to the top. The concentration should not exceed 70%, because above this level the acid will dissolve the methane sulphochloride.

During the process, the reactor is fed with a gaseous mixture containing $CH_4$, $SO_2$, $Cl_2$ and HCl, recycled in molar proportions of approximately 4:4:2:0.3, at an hourly rate of 24.4 cu.m.

The flow rate of 65% sulphuric acid solution is 14,000 l/hr (1.75 l/hr/sq.cm), and its temperature is kept at 20°C. The perforations in the distributor plate in the reactor measure 1 to 1.2 mm in diameter, and they are 6 to 10 mm apart.

In the example described, 140 Kg of decanted product was obtained after 20 hours' functioning, with the following composition:

| | |
|---|---|
| $CH_3SO_2Cl$ | 100 Kg |
| $CH_2H_5SO_2Cl$ | 19 Kg |
| $CHCl_3$ | 2.7 Kg |
| $C_2Cl_6$ | 18 Kg |

Conversion rates were:

$CH_4$: 100 Kg $CH_3SO_2Cl$, corresponding to 14 Kg $CH_4$
Actual consumption: 32 Kg
Conversion rate: $14/32 \times 100 = 44\%$

$SO_2$: 100 Kg $CH_3SO_2Cl$ corresponding to 56 Kg $SO_2$
Actual consumption: 120 Kg
Conversion rate: $56/120 \times 100 = 46.5\%$

$Cl_2$: 100 Kg $CH_3SO_2Cl$ corresponding to 31 Kg $Cl_2$
Actual consumption: 263 Kg
Conversion rate: $31/263 \times 100 = 12\%$

In another example, of the preparation of methane sulphochloride, a gaseous mixture containing $CH_4$, $SO_2$, $Cl_2$ and HCl, recycled in molar proportions of approximately 4:4:0.3 and 0.3 was fed into the reactor.

121.8 Kg of decanted product was obtained, with the following composition:

| | |
|---|---|
| $CH_3SO_2Cl$ | 100 Kg |
| $C_2H_5SO_2Cl$ | 21.8 Kg |

Conversion rates were:

$CH_4$: 100 Kg $CH_3SO_2Cl$ corresponding to 14 Kg $CH_4$
Actual consumption: 16.6 Kg
Conversion rate: $14/16.6 = 84.3\%$

$SO_2$: 100 Kg $CH_3SO_2Cl$ corresponding to 56 Kg $SO_2$
Actual consumption: 332.8 Kg
Conversion rate: $56/332.8 = 16.8\%$

$Cl_2$: 100 Kg $CH_3SO_2Cl$ corresponding to 31 Kg $Cl_2$
Actual consumption: 103.7 Kg
Conversion rate: 31/103.7=29.9%

This new process can also be used in the photochemical preparation of 2,2 - trichloroethylene from vinyl chloride, in accordance with the reaction:

$$CH_2{=}CHCl+Cl_2 \xrightarrow{h\nu} CH_2Cl-CHCl_2$$

This reaction, which involves a risk of explosion, is made possible by the use of the reactor in which the liquid phase is finely distributed during the operation. This liquid phase may be either the product itself after degassing, or a sulphuric or hydrochloride aqueous inorganic phase.

Another application of this new process is in photochemical preparation of mercaptan from gaseous olefins and $H_2S$, in accordance with the reaction:

$$R-CH{=}CH_2+H_2S \xrightarrow{h\nu} R-CH_2-CH_2-SH$$

The liquid phase may be a polar organic phase, such as an inferior alcohol or glycol, or an aqueous solution of inorganic acids or salts, which will not dissolve the olefins or mercaptans.

WHAT WE CLAIM IS:—

1. A photochemical process for preparing a halogen-substituted hydrocarbon from an olefin and a halogen source by an addition reaction, a sulphohalide-substituted hydrocarbon from a hydrocarbon, $SO_2$ and a halogen, and a mercaptan from an olefin and $H_2S$ by an addition reaction, wherein all the reactants are passed through an irradiated reactor in gaseous form, in contact with a dispersed liquid phase comprising at least one liquid which is inert and is substantially incapable of dissolving the reactants, the liquid phase being fed in at the top of the reactor in the form of a shower of droplets and, passed through the reactor, so that it reaches the whole of the section of the reactor which is in contact with the gaseous mixture, the liquid which has passed through the reactor being treated to separate out the products of the reaction.

2. A process according to Claim 1, wherein the liquid from which the reaction products have been removed is passed through a heat exchanger and recycled to the reactor.

3. A process as defined in Claim 1 or Claim 2 in which the liquid phase cannot dissolve the reaction product.

4. A process as defined in any preceding Claim for the preparation of methane sulphochloride, in which the reactants forming the gaseous mixture are methane, sulphur dioxide and chlorine, the liquid phase consists of a sulphuric acid solution, the liquid phase drawn off at the base of the reactor passes into a degassing decanter, where gaseous reactants, the phase containing methane sulphochloride and the sulphuric phase are separated, the sulphuric acid phase being reintroduced into the reactor after passing through a heat exchanger, which reduces its temperature to approximately 20°C.

5. A photochemical process according to Claim 1 and substantially as herein described with reference to the Example.

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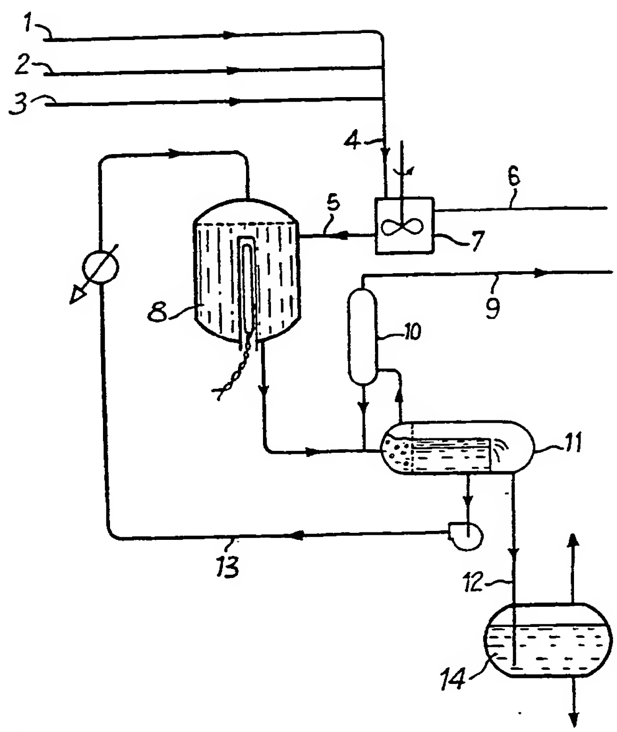
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